


PTO 02-3220

CY=JP DATE=19960620 KIND=A
PN=09-3028433

INK-JET RECORDING PAPER
[In'ku Jetto Kiroku Yoshi]

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Washington, D.C.

June 2002


Translated by: FLS, Inc.

Best Available Copy

PUBLICATION COUNTRY	(10):	JP
DOCUMENT NUMBER	(11):	09-3028433
DOCUMENT KIND	(12):	A
	(13):	PUBLISHED UNEXAMINED PATENT APPLICATION (Kokai)
PUBLICATION DATE	(43):	09-3028433 [WITHOUT GRANT]
PUBLICATION DATE	(45):	[WITH GRANT]
APPLICATION NUMBER	(21):	08-159759
APPLICATION DATE	(22):	19960620
PRIORITY DATE	(32):	
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	
DOMESTIC CLASSIFICATION	(52):	
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
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TITLE	(54):	Ink-jet Recording Paper
FOREIGN TITLE	[54A]:	In'ku Jetto Kiroku Yoshi

1. Name of this Invention

Ink-jet Recording Paper

2. Claims

[Claim 1]

Ink-jet recording paper with the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and hydrophillic binder formed on a base material where the weight ratio of solid particles to the hydrophillic binder of said ink absorption layer is 2 - 200 times,

polyol with 300 or less molecular weight and having at least two hydroxyl groups in a molecule is added to the base material for 2 - 8 wt% of the entire hydrophilic binder existing on the ink-absorption side of the base material.

[Claim 2]

In Claim 1, said solid particle is either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

[Claim 3]

In Claim 1 or 2, said hydrophillic binder contains at least one kind of material selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol.

[Claim 4]

Ink-jet recording paper with the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and at least one kind of polyvinyl alcohol selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol, where the weight ratio of solid particles to the

* Numbers in the margin indicate pagination in the foreign text.

total quantity of said selected polyvinyl alcohol is 2 - 200 times;

said layer containing solid particles includes at least one kind of polyvinyl alcohol selected from at least two kinds of polyvinyl alcohol and/or polyvinyl derivatives where the average polymerization ratio of one material is at least twice as high as that of another material.

[Claim 5]

In Claim 4, said solid particle is selected from either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm. /2

[Claim 6]

Ink-jet recording paper with the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and hydrophillic binder formed on a base material where the weight ratio of solid particles to the hydrophillic binder of said ink absorption layer is 2 - 200 times,

said ink absorption layer contains 10 - 80 wt% of oil drops per total amount of solid particles.

[Claim 7]

In Claim 6, the average particle diameter of said oil drops is 0.05 - 0.5 μm .

[Claim 8]

In Claim 6 or 7, said solid particle is selected from either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

[Claim 9]

In Claim 7 or 8, said hydrophilic binder is at least one kind of material selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol.

[Claim 10]

Ink-jet recording paper with the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and hydrophillic binder formed on a base material where the weight ratio of solid particles to the hydrophillic binder of said ink absorption layer is 2 - 200 times,

said ink absorption layer contains anionic surface activation agent and cationic surface activation agent.

[Claim 11]

In Claim 10, the weight ratio of said anionic and cationic surface activation agents is 20 : 1 - 1 : 1.

[Claim 12]

In Claim 11, said solid particle is selected from either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

[Claim 13]

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In Claim 10, 11, or 12, said hydrophilic binder is at least one kind of hydrophilic material selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol.

[14]

Ink-jet recording paper with the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and hydrophillic binder formed on a base material where the weight ratio of solid particles to the hydrophillic binder of said ink absorption layer is 2 - 200 times,

said ink absorption layer contains a betain type surface activation agent.

[Claim 15]

In Claim 14, said solid particle is selected from either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

[Claim 16]

In Claim 14 or 15, said hydrophilic binder is at least one kind of material selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol.

[Claim 17]

Ink-jet recording paper with the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and hydrophilic binder formed on a base material where the weight ratio of solid particles to the hydrophilic binder of said ink absorption layer is 2 - 200 times,

said ink absorption layer contains a high molecular anionic surface activation agent having at least 1,000 of molecular weight.

[Claim 18]

In Claim 17, said solid particle is selected from either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

[Claim 19]

In Claim 17 or 18, said hydrophilic binder is at least one kind of hydrophilic material selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol.

[Detailed explanation of this invention]

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[0001] [Industrial Field]

This invention pertains to an ink-jet recording paper used for recording with water-base ink and is particularly associated with an ink-jet recording paper having improved ink absorbency.

[0002] [Conventional Technology]

Ink-jet recording is a technique of recording images and characters by scattering fine ink liquid drops using various mechanisms to adhere onto the recording sheet surface, providing advantages of relatively fast printing, low noise, and easy color production. The problems of nozzle plugging and maintenance associated with this type of printing technique have significantly

improved, allowing the technique to be applied in a wide range of applications, such as various printers, fax machines, computer terminals.

[0003]

The recording sheet for this ink-jet recording method must provide high density printed dots, bright and clear color tone, quick ink absorption to prevent ink flowing and smudging when printed dots overlay with each other, and does not excessively disperse the ink dot in sideways with smooth and crisp dot boundaries.

[0004]

When ink absorption speed is slow, liquid drops cause a crawling phenomenon to for uneven printing when multiple color ink drops overlay with each other, and each color smudges at the color boundaries, thereby significantly lowering the image quality. Therefore, recording sheet must have a high ink absorption capacity.

[0005]

To solve those problems, various methods were developed.

[0006]

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The following describes examples of improved ink-jet recording sheets:

Surface treatment coating is soaked in a low-size raw sheet (Patent No. 52-53012), ink absorbing coating layer is formed over the surface of support material (Patent No. 55-5830), hard silica powder is mixed as pigments in the coat layer (Patent No. 56-157), inorganic and organic pigments are mixed in the sheet (Patent No. 57-107878), sheet having two empty hole distribution peaks (Patent No. 58-110287), sheet having upper/lower layers with numerous porous (Patent No. 62-111782), sheet having monolithic cracks (Patent No. 59-68292, 59-124696 and 60-18383), sheet having a fine powder layer (Patent No. 61-135786, 61-148092, and 62-149745), sheet containing pigments and fine particle silica having specific physical characteristic values (63-252779, 1-108083, 2-136279, 3-65376, 3-27976), sheet containing fine silica particles (e.g., colloidal silica) (Patent No. 57-14091, 60-219083, 60-210984, 61-20797, 61-188183, 5-278324, 6-92011, 6-183134, 7-137431, 7-276789),

and sheet containing alumina hydrate fine particles (Patent No. 2-276671, 3-67684, 3-215082, 3-251488, 4-67986, 4-263983, and 5-16517).

[0007]

Among those ink-jet recording sheets, the sheet having an ink reception layer containing numerous spaces for absorbing and holding the ink (from here, the term "space layer" is used) can provide particularly high quality images, as it has excellent ink absorption capacity without causing boundary smudging.

[0008]

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Furthermore, since those spaces may change their volume sizes due to high temperature/moisture during preservation period, solid fine particles are preferably included in the space to prevent the space-volume variation.

[0009]

To form spaces in which solid fine particles are included, hydrophilic binder must be added beforehand for creating a stable cover film. However, if the ratio of hydrophilic binder to the solid fine particles is too high, the binder may plug the solid particles or spaces formed around the solid fine particles, or this hydrophilic binder itself is swollen during the initial phase of ink absorption period to plug the space layer, worsening the ink absorbency. Therefore, the usable amount of such material is limited.

[0010]

Based on the investigation of the developers of this invention, the ratio of hydrophilic binder additive to the amount of solid fine particles should be approximately 2 - 200 times.

[0011]

However, a layer containing solid fine particles at this high ratio forms fragile film. Particularly, when stored in a low moisture environment, fine cracks occur on the surface of ink absorption layer. When this type of ink-jet recording sheet is used for ink-jet recording, ink spreads along the cracks to form extremely worsened image quality.

[0012] [Problems to be solved by this invention]

This invention was developed to solve those problems. The purpose of this invention is to provide an ink-jet recording sheet that has high ink absorption capacity provided by solid fine particles dispersed in a hydrophilic binder and can provide high quality printing without causing film weakness even after preserved in a low moisture environment.

[0013] [Method to solve the problems]

The purpose of this invention can be achieved by the following method:

[0014]

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Ink-jet recording paper described in Claim 1 providing the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and hydrophilic binder formed on a base material where the weight ratio of solid particles to the hydrophilic binder of said ink absorption layer is 2 - 200 times; polyol with 300 or less molecular weight and having at least two hydroxyl groups in a molecule is added to the base material for 2 - 8 wt% of the entire hydrophilic binder existing on the ink-absorption side of the base material.

[0015]

With the ink-jet recording sheet described in Claim 1, said solid particle is either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

[0016]

With the ink-jet recording sheet described in Claim 1 or 2, said hydrophilic binder contains at least one kind of material selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol.

[0017]

Ink-jet recording paper with the following characteristic as described below:

With an ink-jet recording paper having an ink absorption layer containing solid particles and at least one kind of polyvinyl alcohol selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol, where the weight ratio of solid particles to the total quantity of said selected polyvinyl alcohol is 2 - 200 times; said layer containing solid particles includes at least one kind of polyvinyl alcohol selected from at least two kinds of polyvinyl alcohol and/or polyvinyl derivatives where the average polymerization ratio of one material is at least twice as high as that of another material.

[0018]

With the ink-jet recording sheet described in Claim 4, said solid particle is selected from either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

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[0019]

Ink-jet recording paper with the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and hydrophillic binder formed on a base material where the weight ratio of solid particles to the hydrophillic binder of said ink absorption layer is 2 - 200 times; said ink absorption layer contains 10 - 80 wt% of oil drops per total amount of solid particles.

[0020]

With the ink-jet recording sheet described in Claim 6, the average particle diameter of said oil drops is 0.05 - 0.5 μ m.

[0021]

With the ink-jet recording sheet described in Claim 6 or 7, said solid particle is selected from either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

[0022]

With the ink-jet recording sheet described in Claim 7 or 8, said hydrophilic binder is at least one kind of material selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol.

[0023]

Ink-jet recording paper with the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and hydrophillic binder formed on a base material where the weight ratio of solid particles to the hydrophillic binder of said ink absorption layer is 2 - 200 times; said ink absorption layer contains anionic surface activation agent and cationic surface activation agent.

[0024]

With the ink-jet recording sheet described in Claim 10, the weight ratio of said anionic and cationic surface activation agents /9 is 20 : 1 - 1 : 1.

[0025]

With the ink-jet recording sheet described in Claim 11, said solid particle is selected from either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

[0026]

With the ink-jet recording sheet described in Claim 10, 11, or 12, said hydrophilic binder is at least one kind of hydrophilic material selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol.

[0027]

Ink-jet recording paper with the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and hydrophillic binder formed on a base material where the weight ratio of solid particles to the hydrophillic binder of said ink absorption layer is 2 - 200 times; said ink absorption layer contains a betain type surface activation agent.

[0028]

With the ink-jet recording sheet described in Claim 14, said solid particle is selected from either silica, calcium carbonate,

alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

[0029]

With the ink-jet recording sheet described in Claim 14 or 15, said hydrophilic binder is at least one kind of material selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol.

[0030]

Ink-jet recording paper with the following characteristic:

With an ink-jet recording paper having an ink absorption layer containing solid particles and hydrophilic binder formed on a base material where the weight ratio of solid particles to the hydrophilic binder of said ink absorption layer is 2 - 200 times; said ink absorption layer contains a high molecular anionic surface activation agent having at least 1,000 of molecular weight.

[0031]

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In Claim 17, said solid particle is selected from either silica, calcium carbonate, alumina/alumina hydrate, or magnesium silicate, whose average primary particle diameter is 7 - 80 nm.

[0032]

In Claim 17 or 18, said hydrophilic binder is at least one kind of hydrophilic material selected from polyvinyl alcohol and/or cationic denatured polyvinyl alcohol.

[0033]

The following explains this invention in detail:

[0034]

The solid fine particles included in the ink-jet recording sheet based on this invention can be any conventional solid fine particles commonly used by the industry.

[0035]

Examples of inorganic fine particles used for this purpose are white inorganic pigments, such as light calcium carbonate, heavy

calcium carbonate, magnesium carbonate, kaolin, clay, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc hydroxide, zinc sulfate, zinc carbonate, hydrosulfite, aluminum silicate, diatomaceous, calcium silicate, magnesium silicate, synthetic non-crystal silica, colloidal silica, alumina, colloidal alumina, coagulated boehmite, aluminum hydroxide, lithopone, zeolite, and magnesium hydroxide.

[0036]

Such inorganic fine particles may be uniformly dispersed in the binder while maintaining their primary particle forms, or it may form secondary coagulated particles, being dispersed in a binder.

[0037]

Examples of organic fine particles are polystyrene, polyacrylic acid ester, polymethacrylic acid ester, polyacryl amide, polyethylene, polypropylene, polyvinyl chloride, polyvinilidene chloride, copolymers of those materials, urea resin, and melamine resin.

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[0038]

Since this invention provides a space layer having a relatively high space ratio, the use of inorganic solid fine particles is preferred, where the solid fine particles are preferably selected from silica, calcium carbonate, alumina, alumina hydrate, and magnesium silicate, as those materials can provide high glossiness and image density.

[0039]

As silica type fine particles preferably used in the recording sheet based on this invention, various silica type fine particles known to the industry can be used.

[0040]

Examples of such silica are synthetic silica composed by a wet or vapor-phase method, colloidal silica, and porous silica forming secondary particles which are coagulated primary particles, shaped into desired shape. Examples are synthetic non-crystal silica (Patent No. 55-51583, 56-148583), silica super fine particles synthesized using a vapor phase method (Patent No. 60-204390),

synthetic monolithic silica containing fluorine (Patent No. 60-222282), synthetic monolithic silica surface-treated with a silane coupling agent (Patent No. 60-224580, 62-178384), spherical silica (Patent No. 62-183382, 63-104878), synthetic silica fine particles containing at least 0.5 wt% of Na₂O (Patent No. 63-104878), synthetic silica fine particles having at least 100m²/g of relative surface area (Patent No. 01-115677), synthetic silica fine particles surface-treated with aluminum (Patent No. 62-286787), synthetic silica fine particles surface-treated with Ca, Mg, or Ba, and synthetic silica fine particle having at least 180 ml/g of oil absorption capacity (Patent No. 01-259982), colloidal silica (Patent No. 57-14091), cationic colloidal silica (Patent No. 60-219084, 06-92011, 06-297830, 07-81214), connected spheres of or branched silica (Patent No. 05-278324, 07-81214).

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[0041]

However, in order to obtain a high glossiness and spacial volume, super fine silica particles having average particle diameter of 7 - 80 nm are preferred. This type of particles may be surface-denatured with cation or may be surface-treated with Al, Ca, Mg, and BA.

[0042]

Examples of calcium carbonate preferably used in this invention are light calcium carbonate having a specific relative surface area (Patent No. 57-12486, 57-129778, 58-55283, 61-20792), needle-like calcium carbonate (Patent No. 63-57277 and 4-250091), calcium carbonate fine particles forming secondary particles with coagulated specific needle-like primary particles (Patent No. 3-251487), needle-like rhombic aragonite calcium carbonate having a specific oil absorption quantity (Patent No. 4-250091 and 4-260092), and spherical precipitating calcium carbonate (Patent No. 7-40648).

[0043]

In this case, the use of calcium carbonate fine particles having approximately 7 - 80 nm particle diameter is preferred.

[0044]

The preferred magnesium silicate may be in any shape, such as monolithic particles, spheres, or plates, where plate-shape is preferred. The average particle diameter of plate-like magnesium

silicate is expressed as the diameter of a circle obtained by converting the measured average reflection area of the plate into a circle, where particles with 7 - 80 nm average diameter are preferred.

[0045]

The alumina or alumina hydrate used in this invention may be crystal or non-crystal in any shape, such as monolithic particle, spherical particle, or needle particle.

[0046]

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To measure the average diameter of each type of inorganic solid fine particles described above, average reflection area is measured using an electronic microscope and converted into a circle; then, the diameter of the circle is used as the average diameter of particles.

[0047]

Solid fine particles used in this invention are preferably primary particles having 7 - 80 nm of average particle diameter.

[0048]

The layer including solid fine particles must contain a hydrophilic binder for forming a film.

[0049]

Examples of hydrophilic binder used for producing ink-jet recording paper based on this invention are gelatine or gelatine derivative, polyvinyl pyrrolidone (preferably average molecular weight exceeds approximately 200,000), bulran, polyvinyl alcohol or its derivative (preferably average molecular weight exceeds approximately 20,000), polyethylene glycol (preferably average molecular weight exceeds approximately 100,000), carboxy cellulose, hydroxy ethyl cellulose, dextran, dextrine, polyacrylic acid and its salt, agar, k-carrageenan, λ -carrageenan, ι -carrageenan, quisantene rubber, rohcast bean rubber, alquic acid, Arabian rubber, bulran, polyalkylene oxide copolymer (Patent No. 7-195826, 7-9757), water-soluble polyvinyl butylal, and vinyl monomer containing a carboxyl group and sulfonic acid group or copolymer consisting of repetitious those vinyl monomers. Those hydrophilic binders may be used alone or mixed together.

[0050]

Among those materials, it should contain at least polyvinyl alcohol or cation-denatured polyvinyl alcohol for providing improvements over moisture-absorption of film, stickiness caused by high moisture, and smudged ink die.

[0051]

/14

Preferred polyvinyl alcohol should have average polymerization ratio of 500 - 4000, and saponification ratio is preferably 70 - 100%, more preferably 80 - 90%.

[0052]

Preferred cation-denatured polyvinyl alcohol can be obtained by saponifying a copolymer of ethylene type unsaturated monomer having a cation group and vinyl acetic acid.

[0053]

Examples of ethylene type unsaturated monomer having a cation group and vinyl acetic acid are trimethyl-(2-acryl amide-2,2-dimethyl ethyl) ammonium chloride, trimethyl-(3-acrylamide, 3,3-dimethyl propyl) ammonium chloride, N-vinyl imidazol, N-vinyl-2-methylimidazol, N-(3-dimethyl aminopropyl) methacryl amide, hydroxyethyl trimethyl ammonium chloride, trimethyl-(-methacryl aide propyl) ammonium chloride, and N-(1,1-dimethyl-3-dimethyl aminopropyl) acryl amide.

[0054]

The ratio of monomer containing a cation-denatured group of cation-denatured polyvinyl alcohol should be 0.1 - 10 mol % for the total amount of vinyl acetic acid, where the ratio of 0.2 - 5 mol is preferred.

[0055]

The polymerization ratio of cationic-denatured polyvinyl alcohol should be 500 - 4000, preferably 1000 - 4000.

[0056]

The saponification ratio of vinyl acetic acid group is preferably 60 - 100 mol%, more preferably 70 - 99 mol%.

[0057]

The layer containing the solid fine particles based on this invention preferably contains polyvinyl alcohol and/or cation-denatured polyvinyl polymer at a ratio of 60 wt% or higher to the amount of hydrophilic binder of the hydrophilic layer, where the ratio of 80 - 100 wt% is more preferred. /15

[0058]

With the ink-jet recording sheet based on this invention, the weight ratio of solid fine particles forming a space layer to the hydrophilic binder should be 2 - 200 times. If it is below 2 times, the relative spacial ratio becomes insufficient to cause various problems, such as excessive film thickness for complete absorption of maximum ink quantity; or, the hydrophilic binder swells during ink-absorption to lower the ink-absorption speed of space layer.

[0059]

On the other hand, if it exceeds 200 times, the film becomes too fragile even if it is treated with various methods (described later) to produce high quality images.

[0060]

Preferred ratio is 2.5 - 100 times, more preferably 3 - 50 times.

[0061]

Due to particularly high ratio of solid fine particles to the binder quantity in the space layer of the ink-jet recording sheet, the film tends to be fragile. To improve this problem, at least one of the following conditions must be satisfied:

① Polyol having at least two hydroxyl groups in the molecule with 300 of maximum molecular weight is included for an amount of 2 - 8 wt% per entire hydrophilic binder existing on the ink-absorption layer side of the support body.

② The layer including solid fine particles contains at least one kind of polyvinyl alcohols selected from at least two kinds of polyvinyl alcohols and/or their derivatives where the average polymerization ratio of one polyvinyl alcohol is at least twice as

high as the other polyvinyl alcohol.

③ The ink-absorption layer contains 10 - 80 wt% of oil drops per total solid fine particles.

④ The ink-absorption layer contains an anionic and cationic surface activation agents.

⑤ The ink-absorption layer contains betain type surface activation agent.

⑥ The layer contains high molecular anionic surface activation agent where its molecular weight exceeds 1000.

[0062]

/16

In condition ①, examples of polyol having at least two hydroxyl groups in molecule whose weight does not exceed 300 are ethylene glycol, diethylene glycol, triethylene glycol, tetra ethylene glycol, propylene glycol, glycerine, 1,6-hexane diol, 1,2-cyclohexane diol, 1,2,3-butane triol, and 1,2,4-butane triol, polyethylene glycol or polypropylene glycol whose maximum molecular weight is 300.

[0063]

The amount of those polyol materials should be 2 - 8 wt% per entire hydrophilic binder on the ink absorption layer side of the support body. If it is less than 2 wt%, the film-strengthening effect cannot be provided, whereas an amount exceeding 8 wt% results in high moisture-absorption of the film during preservation to cause adhesion with the back surface.

[0064]

In condition ②, with said at least two kinds of polyvinyl alcohols and/or polyvinyl alcohol derivatives whose one average polymerization is twice as high as that of the other one, such two kinds of polyvinyl alcohols/derivatives may be the same materials. Also, their compositions may be different. At least one kind of material is preferably polyvinyl alcohol of high molecular weight.

[0065]

Polyvinyl alcohol derivative is preferably a cation-denatured polyvinyl alcohol, where the average polymerization ratio of the

material having a low molecular count should be less than 500, particularly preferably within a range of 200 - 400. On the other hand, the average polymerization ratio of the material having a high molecular count is preferably at least 1000, preferably 1500 - 4000.

[0066]

The ratio of low molecular count material to the high molecular count material should be 0.1 - 20 wt%, preferably 0.5 - 10 wt%.

[0067]

/17

In condition ③, the preferred material of oil drops is an hydrophobic organic compound where the water-solubility of such oil drops in the ink-absorption layer at room temperature is preferably less than 0.1%, more preferably less than 0.01 wt%. Examples of such material are phthalic acid ester (dibutyl phthalate, dioctyl phthalate, di-isodecyl phthalate), phosphoric acid ester (tricredyl phosphate), fatty acid ester (stearic acid butyl, cebasic acid bis (2-ethyl hexyl), ethylene glycol distearate), amide (N,N-diethyl lauryl amide, N,N-diethyl-2-(2,5-di-t-amyl phenoxy) butane amide), ether (ethylene glycol dibutyl ether, decyl ether), and liquid paraffin. Those materials may be used alone or mixed together.

[0068]

To add said oil drops, they are preferably emulsified and dispersed using a high speed homogenizer. The preferred oil drop size is 0.05 - 0.5 μm , more preferably 0.1 - 0.4 μm .

[0069]

The amount of said oil drops should be 10 - 80 wt% per the amount of solid fine particles included in the space layer. If it is below 10 wt%, the film strength cannot be improved, whereas an amount exceeding 80 wt% lowers the ink-absorption capacity.

[0070]

The preferred oil drop quantity is 20 - 60 wt% per the amount of solid fine particles.

[0071]

In condition ④, the anionic/cationic surface activation agents included in the ink-absorption layer may be any conventional materials.

[0072]

The ratio of cationic agent and anionic agent should be 1 : 10 - 5 : 1, more preferably 1 : 10 - 2 : 1. The total amount of surface activation agents should be 0.2 - 20 wt%, preferably 0.5 - 10 wt% of the total solid fine particles in the ink-jet recording sheet.

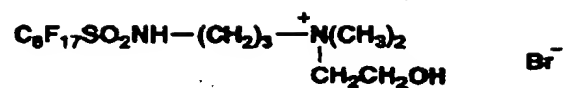
[0073]

/18

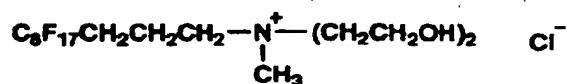
The following shows the practical examples of cationic surface activation agents:

[0074] [Chemical 1]

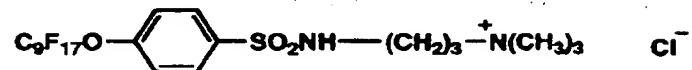
KS-1



KS-2



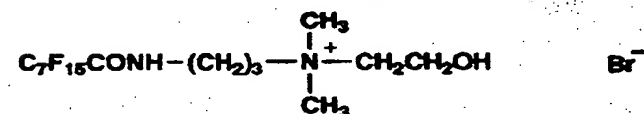
KS-3



KS-4



KS-5



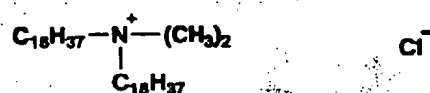
KS-6



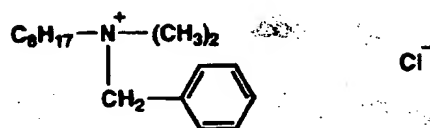
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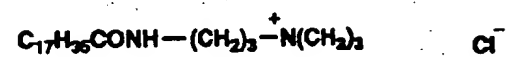
KS-8



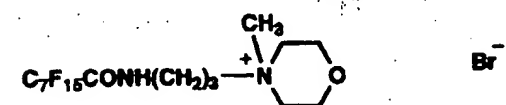
KS-9



KS-10



KS-11



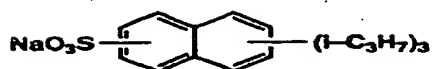
[0076]

The following shows the practical examples of anionic surface activation agents:

[0077] [Chemical 3]

/20

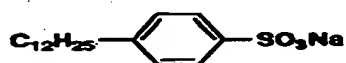
AS-1



AS-2



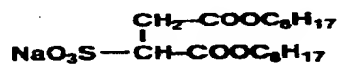
AS-3



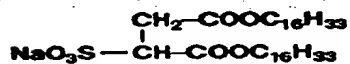
AS-4



AS-5



AS-6



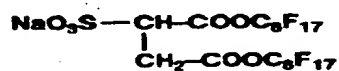
AS-7



AS-8



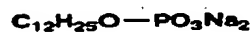
AS-9



AS-10



AS-11

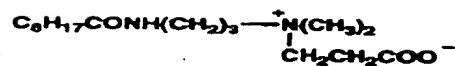


[0078]

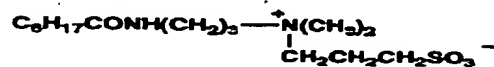
/21

In condition ⑤, the betain surface activation agent included in the ink absorption layer is an agent containing at least anionic and cationic groups in its molecule. The following shows the practical examples:

BS-1



BS-2



BS-3



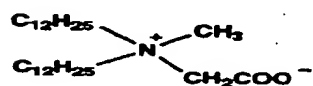
BS-4



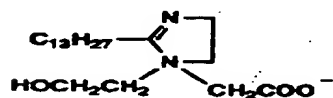
BS-5



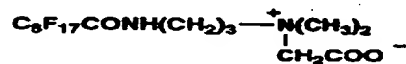
BS-6



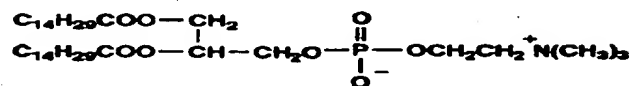
BS-7



BS-8



BS-9



[0080]

/23

The amount of said betain surface activation agent should be 0.1 - 20 wt%, preferably 0.2 - 10 wt% of the total solid fine particle quantity in the recording sheet.

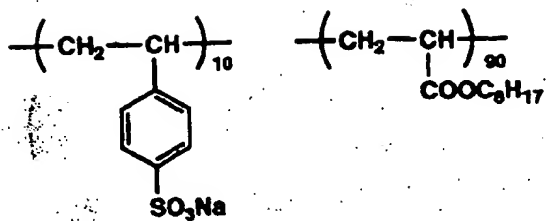
[0081]

In condition ⑥, the high molecular anionic surface activation agent (molecular weight is 1000 or higher) is a polymer or condensed material prepared from at least one substance selected from carboxylic acid, sulfonic acid or phosphoric acid group, monomer having at least four aliphatic groups, and other monomers used if necessary; or, a polymer or condensed material prepared from monomer having at least one of carboxylic acid, sulfonic acid, and phosphoric acid group, monomer having at least four aliphatic groups, and other monomers used if necessary.

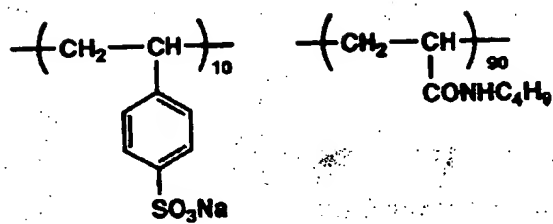
[0082]

The following shows the practical compounds. Note that the monomer ratio designates a mol ratio.

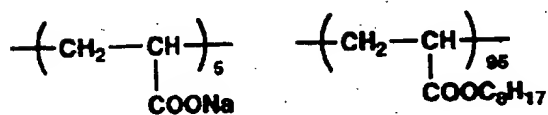
PS-1



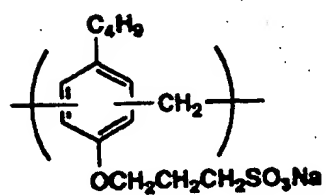
PS-2



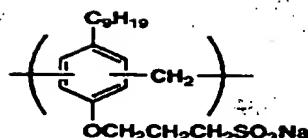
PS-3



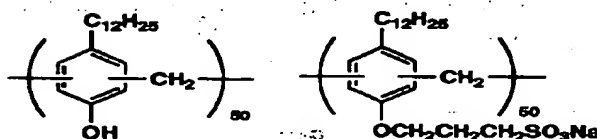
PS-4



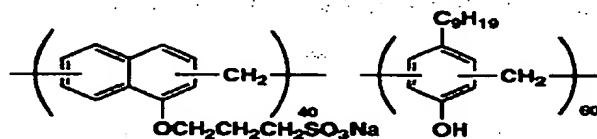
PS-5



PS-6



PS-7



[0085]

The amount of said high molecular anionic surface activation agent should be 0.1 - 20 wt%, preferably 0.2 - 5 wt% per total amount of solid fine particles in the recording sheet.

[0086]

The ink-jet recording sheet based on this invention containing ink-absorption layer consisting of said solid fine particles and hydrophilic binder may also contains a hydrophilic binder layer. Such binder layer does not need to contain solid fine particles. However, if it is not a space layer, and when it is placed away from the support body than the solid fine particle layer, the dry film thickness should be 2 μm or less, preferably 1.5 μm or less. /26

[0087]

The ink reception layer side of the recording sheet can contain various additives if necessary.

[0088]

Examples of such additives are ultraviolet ray absorption agents (Patent No. 57-74193, 57-87988, and 62-261476), anti color fading agents and various surface activation agents of anion, cation, or nonion (Patent No. 57-74192, 57-87989, 60-72785, 61-146591, 1-95091, and 3-13376), fluorescent whitener, pH adjuster (e.g., sulfuric acid, phosphoric acid, succinic acid, sodium hydroxide, potassium hydroxide, potassium carbonate), defoaming agent, lubricant (e.g., de-ethylene glycol), antiseptic agent, viscosity increasing agent, film-hardening agent, charge prevention agent, matting agent.

[0089]

As a film-hardening agent, organic or inorganic agent may be used. Examples of such materials are chrome alum, formaldehyde, glyxyal, epoxy compounds, vinyl sulfonic compounds, acryloyl compounds, s-thiazine compounds, N-methylol compounds, carbo di imide compounds, and ethylene imino compounds.

[0090]

Although the amount of solid coating quantity on the ink recording surface side of the recording sheet is not particularly limited, it is preferably 10 - 40 g/m², more preferably 20 - 30 g/m². To prevent curling after image formation, the coating should be made as thin as possible.

[0091]

/27

The optional layer on the recording side of the sheet may contain an anti-hydration agent for printed images. Examples are polycationic high molecular electrolyte (Patent No. 56-84992), basic latex polymer (Patent No. 57-36692), polyaryl amine (Patent No. 4-15744, 61-58788, and 62-174184), and alkali metallic weak acid salt (Patent No. 61-47290). Several of those materials may be added together.

[0092]

The support body of the recording sheet may be any conventional material.

[0093]

Examples of clear support body are a film, plate, and glass plate consisting of a polyester resin, diacetate resin, triacetate resin, acryl resin, polycarbonate resin, polyvinyl chloride resin, polyimide resin, cellophane, or celluloid, where a material having resistance to the focused heat to stand for the use of OHP is preferred (polyethylene terephthalate is most preferred.) The thickness of this type of film should be approximately 10 - 200 μm .

[0094]

Examples of support body not required to be transparent are sheet or plate consisting of a regular paper, synthetic paper, resin coating paper, cloth, wood, or metal, and materials prepared by making the clear substances described above non-transparent. As a non-transparent support body, the preferred materials are resin-coated paper (i.e., RC paper) containing a polyolefin resin coat layer including white pigment in at least one side of base sheet and white paper prepared by adding white pigment to polyethylene terephthalate.

[0095]

The effectiveness of this invention can be magnified when the support body is not water-absorbing, where particularly preferred materials are a plastic support body (e.g., clear/non-clear polyethylene terephthalate) or support body prepared by coating the surface of raw paper with a hydrophobic resin such as polyethylene./28

[0096]

To enhance the adhesive strength between the support body and ink reception layer, the support body is preferably treated by a corona charging or under-coating process prior to ink reception layer coating. Furthermore, the recording sheet based on this invention does not need to be non-colored and may be colored.

[0097]

When producing the sheet based on this invention, a method of coating each hydrophilic layer containing an ink reception layer over a support body may be any conventional technique. Preferred method is that a coating liquid containing a sol/gel convertible hydrophilic binder such as gelatine is coated over a support body and dried. In this case, several hydrophilic binder layers may be coated simultaneously. The coatings of hydrophilic binder layers are preferably performed with one coating.

[0098]

Preferred example is that ink reception layer containing a sol/gel convertible hydrophilic binder such as gelatine described in Patent No. 6-64306 is coated over a support body, cooled, made into a gel, and dried using a cold-drying method.

[0099]

During this process, the coated liquid is preferably dried by the heat which does not re-melt the coated liquid. Normally, after coating, the moisture is evaporated at room temperature - 30°C, and the surface is heated to 40°C - 50°C for complete drying.

[0100]

Although a sol/gel non-convertible coating liquid may be used, an additional care is required to allow the film surface to be uniformly dried.

[0101]

Preferred coating methods are roller coating, rod bar coating, air knife coating, spray coating, curtain coating, and extrusion /29 coating using a whopper (U.S. Patent No. 2,681,294).

[0102]

The water-base ink in this invention is a recording liquid consisting of coloring agents described below and liquid medium, and other additives. Coloring agents may be any known water-soluble dyes, such as direct dye, acid dye, basic dye, reactive dye, or food coloring dye.

[0103]

Water-base ink solvents may be water or water-soluble various organic solvents. Examples are alcohols, such as methyl alcohol, isopropyl alcohol, n-butyl alcohol, tert-butyl alcohol, and isobutyl alcohol; amides, such as dimethyl form amide and dimethyl acetamide; ketone or ketone alcohol, such as acetone, deacetone alcohol; ether, such as tetrahydrofuran, dioxane; polyalkylene glycol, such as polyethylene glycol, polypropylene glycol; polyvalent alcohol, such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, 1,2,6-hexane triol, thio di glycol, hexylene glycol, diethylene glycol, glycerine, triethanol, and amine; low class alkyl ether of polyvalent alcohol, such as triethylene glycol monobutyl ether.

[0104]

Among those water-soluble organic solvents, polyvalent alcohol (e.g., diethylene glycol, triethanol amine, and glycerine) and low class alkyl ether of polyvalent alcohol (e.g., triethylene glycol monobutyl ether) are preferred.

[0105]

Examples of other water-base ink additives are pH adjuster, metal sealer, anti-fungus agent, viscosity adjuster, surface tension adjuster, moistening agent, surface activation agent, and antiseptic agent.

[0106]

/30

The water-base ink liquid should have the surface tension of 25 - 60 dyn/cm, preferably 30 - 50 dyn/cm, for providing satisfactory wetness to the recording sheet.

[0107] [Operational examples]

the following explains the operational examples of this invention. Note that this invention is not limited to those examples. "%" in the examples designates "dried weight %" unless noted. Adding amount designates the quantity per 1 m² of recording sheet.

[0108] Operational example 1:

Coating liquid 1 described below (wetted swollen film thickness = 150 μm) was coated over the recording surface of the paper support body (thickness = 140 μm ; 7 wt% of anatase type titanium dioxide is added in the polyethylene layers on both sides of the sheet; a layer containing 4.2 g/m² of alkali-treated gelatine and film-hardening agent is formed over the back surface of the recording sheet) prepared by coating polyethylene over both surfaces of a 100 g/m² of raw sheet. Then, after the film was dried, the same liquid was coated and dried to form a space layer.

[0109] [Coating liquid 1]

Purified water	980 ml
Polyvinyl alcohol (PVA 3500) whose average polymerization ratio = 3500 (saponification ratio = 94%)	48.0 g
Surface activation agent 1 (AS-1)	1.2 g

Coating liquid 2 described below was coated over the prepared coated surface (wetted swollen film thickness = 8 μm) and dried to prepare ink-jet recording sheet - 1.

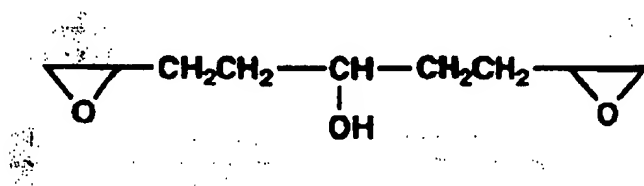
[0110] [Coating liquid 2]

/31

Purified water	800 ml
(Amino group sealing ratio = approx. 88%)	
Polyvinyl pyrrolidone (K-90)	25.0 g
Polyethylene oxide (average molecular weight = approx. 150,000)	12.0 g
Surface activation agent 2 (AS-5)	0.7 g
Film-hardening agent - 1	2.1 g

[0111] [Chemical 7]

Film-hardening agent - 1:



[0112]

Next, various additives or dispersed substances described in Table 1 were added to ink-jet recording sheet - 1 to prepare ink-jet recording sheets 2 - 20.

[0113]

Each additive was added as a water solution or solvent. However, the amount of purified water was adjusted to fix the total amount of coating liquid.

[0114]

Said surface activation agent - 1 was not added to the ink-jet recording sheets 17 - 20.

Recording sheet	Additives/dispersed substances
2	DEG 0.15 g
3	DEG 0.30 g
4	DEG 0.60 g
5	DEG 1.2 g
6	PEG 200 0.6 g
7	PEG 500 0.6 g
8	PVA 300 0.5 g
9	PVA 500 0.5 g
10	PVA 1000 0.5 g
11	PVA 2300 0.5 g
12	LP dispersion liquid 60 ml
13	LP dispersion liquid 250 ml
14	LP dispersion liquid 650 ml
15	KS 1 (2% solution) 20 ml
16	KS 2 (2% solution) 20 ml
17	BS 1 (2% solution) 20 ml
18	BS 2 (2% solution) 20 ml
19	PS 1 (2% solution) 20 ml
20	PS 2 (2% solution) 20 ml

DEG: Diethylene glycol

PEG 200: Polyethylene glycol (average molecular weight = 200)

PEG 500: Polyethylene glycol (average molecular weight = 500)

PVA 300: Polyvinyl alcohol (average molecular weight = 300)

PVA 500: Polyvinyl alcohol (average molecular weight = 500)

PVA 1000: Polyvinyl alcohol (average molecular weight = 1000)

PVA 2300: Polyvinyl alcohol (average molecular weight = 2300)

LP dispersion liquid: Liquid paraffin was emulsified and dispersed in AS-10.05% and PVA 3500 0.1% content under the existence of acetic acid ethyl; liquid paraffin density = 8%; average particle diameter = approx. 4 μ m

Each recording sheet was tested using an ink-jet printer (MJ-900C, product of Seiko Epson) and the results were evaluated:

[0117]

(1) Ink absorption characteristic:

Yellow and cyan (maximum ink quantity = 40%) were evenly ejected for recording. The red color reflection density of the colored area was measured for 20 points using a micro densitometer (aperture = 200 $\mu\text{m}\phi$). The standard deviation of density variation was acquired and divided by the average reflection density to obtain the ink absorbency. The value becomes low when the absorbency is strong to form an even image, and becomes high with low absorbency, as each ink drops cause beading.

[0118]

(2) Film fragility:

Each recording sheet was preserved for one whole day at 25°C and 20% of relative humidity while the sheet was made into a circular tube (60 mm diameter), setting the printed surface outside. Then, the surface cracking was observed using a magnifier.

[0119]

- ◎: No crack was observed through a magnifier.
- : Although some cracks were observed through a magnifier, the image quality was not affected.
- △: Although no crack was visually observed, cracks were observed through a magnifier. Image was affected by cracks.
- X: Cracks were visually observed, significantly affecting the image quality.

[0120]

(3) Adhesiveness:

10 samples were piled without printing, on to which 1 Kg/100 cm^2 of weight was given, and stored for a week at 40°C and 80% of relative humidity.

[0121]

/34

After peeling the samples, the back surface condition was observed to evaluate the adhesiveness.

[0122]

O: No adhesion was observed.

Δ: Partially adhered.

X: Strong force was needed for peeling. The surfaces were adhered.

The obtained results are shown in Table 2.

[0123] [Table 2]

/35

Recording sheet	Ink absorbency	Cracking	Adhesion
1 (Comparison example)	0.10	X	O
2 (Comparison example)	0.11	Δ	O
3 (Operational example)	0.11	O	O
4 (Operational example)	0.13	O	O
5 (Comparison example)	0.15	O	X
6 (Operational example)	0.11	O	O
7 (Comparison example)	0.11	Δ	O
8 (Operational example)	0.12	O	O
9 (Operational example)	0.12	O	O
10 (Operational example)	0.12	O	O
11 (Comparison example)	0.11	Δ	O
12 (Comparison example)	0.12	Δ	O
13 (Operational example)	0.13	O	O
14 (Comparison example)	0.19	O	Δ
15 (Operational example)	0.13	O	O
16 (Operational example)	0.11	O	O
17 (Operational example)	0.14	O	O
18 (Operational example)	0.15	O	O
19 (Operational example)	0.14	O	O
20 (Operational example)	0.13	O	O

[0124]

As shown in the table, the ink-jet recording sheets 2 - 6, 8 - 10, 13 -, 16 - 20 all exhibited high ink absorbency and excellent preservation characteristic without causing any crack when stored in humid area.

[0125]

/36

On the other hand, recording sheets - 2 having a small amount of DEG caused cracks, thereby confirming the necessary amount for preventing cracking to produce high quality image. Also, an excessive amount of DEG (sheet -5) causes increased adhesiveness.

[0126]

With the recording sheet 7 containing polyol having 300 or higher molecular weight, sheet 11 having a insufficient molecular weight of PVA, and sheet 12 containing an insufficient amount of oil drops did not provide sufficient crack-resistance effect. Furthermore, an excessive amount of oil drops (sheet 14) lowered the ink absorbency and adhesion resistance.

[0127] Operational example 2:

Ink-jet recording sheets 1 - 20 and 20 - 40 were prepared in the same manner as described in Operational example 1 except that coating liquid 1 was changed to coating liquid 2, and additives shown in Table 3 were used. The result were evaluated using the same methods as described above.

[0128] [Coating liquid 1-a]

Purified water	920 ml
Calcium carbonate fine particles (average particle diameter = approx. 0.03 μ m)	120 g
Polyvinyl alcohol - polymerization ratio = 3500 (saponification ratio = 90%)	6.2 g
Surface activation agent 1 (AS-1)	1.0 g

Recording sheet	Additives/dispersed substances
22	Glycerine 0.15 g
23	Glycerine 0.30 g
24	Glycerine 0.60 g
25	Glycerine 1.2 g
26	PEG 200 0.6 g
27	PEG 500 0.6 g
28	PVA 300 0.5 g
29	PVA 500 0.5 g
30	PVA 700 0.5 g
31	PVA 1000 0.5 g
32	DIDP dispersion liquid 60 ml
33	DIDP dispersion liquid 250 ml
34	DIDP dispersion liquid 650 ml
35	KS 1 (2% solution) 20 ml
36	KS 3 (2% solution) 20 ml
37	BS 1 (2% solution) 20 ml
38	BS 3 (2% solution) 20 ml
39	PS 3 (2% solution) 20 ml
40	PS 4 (2% solution) 20 ml

DEDP dispersion liquid: Liquid paraffin was replaced with di-isodecyl phthalate. Also, dispersing PVA was adjusted to equal quantity of 1700.

[0130]

The obtained testers were evaluated in the same manner as described above. The results are shown in Table 4.

Recording sheet	Ink absorbency	Cracking	Adhesion
21 (Comparison example)	0.14	X	O
22 (Comparison example)	0.15	Δ	O
23 (Operational example)	0.15	O	O
24 (Operational example)	0.16	O	O
25 (Comparison example)	0.18	O	X
26 (Operational example)	0.13	O	O
27 (Comparison example)	0.14	Δ	O
28 (Operational example)	0.14	O	O
29 (Operational example)	0.13	O	O
30 (Operational example)	0.14	O	O
31 (Comparison example)	0.15	Δ	O
32 (Comparison example)	0.14	Δ	O
33 (Operational example)	0.15	O	O
34 (Comparison example)	0.23	O	Δ
35 (Operational example)	0.14	O	O
36 (Operational example)	0.15	O	O
37 (Operational example)	0.16	O	O
38 (Operational example)	0.15	O	O
39 (Operational example)	0.16	O	O
40 (Operational example)	0.16	O	O

[0132]

As shown in Table 4, when calcium carbonate fine particles were used as solid particles, the same results could be obtained.

[0133] Operational example 3:

/39

Testers were prepared using the same method as described in Operational example 2 except that calcium carbonate fine particles were replaced with magnesium silicate fine particles (average particle diameter = 30 nm, thickness = 1 nm). The result were evaluated using the same methods as described above.

[0134]

The same effectiveness as obtained in Operational example 2 was produced.

[0135] [Effectiveness of this invention]

As confirmed in the operational examples, the ink-jet recording sheets based on this invention has high ink absorbency with solid particles dispersed in a hydrophilic binder. Also, when stored in low humidity, the film fragility or film adhesion do not occur, allowing the sheets to produce high quality images.

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